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**(54) THICK FILM OF TAPE-LIKE OXIDE SUPERCONDUCTOR AND METHOD FOR MANUFACTURING IT**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thick film of tape-like oxide superconductor by a MOD(metal organic deposition) method using TFA(trifluoroacetate).

SOLUTION: A mixed solution of TFA salts, which contains a prescribed molecular ratio of metal elements composing a RE-base oxide superconductor, is applied onto an IBAD composite substrate, calcine-processed to obtain a precursor, and the precursor is heated for crystallization to give a thick film of tape-like oxide superconductor. Several layers of the precursor are formed on the substrate, and by performing the calcination processing for except at least the most outer layer of the precursor within the temperature range of 250 to 350° C, and the steam partial pressure of an inducing gas in crystallization heat treatment atmosphere before crystallization of the most outer layer of the precursor within the range of 0.5 to 3.2 vol.% in order to easily obtain the thick film of a tape-like oxide superconductor.

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(54) 【発明の名称】 厚膜テープ状酸化物超電導体及びその製造方法

(57) 【要約】

【課題】 T F Aを用いたMOD法により厚膜のテープ状酸化物超電導体を提供する。

【解決手段】 R E系酸化物超電導体を構成する各金属元素を所定のモル比で含むT F A塩の混合溶液をI B A D接合基板上に塗布し、仮焼熱処理を施した前駆体に結晶化熱処理を施した酸化物超電導体において、基板上に前駆体を複数層形成するとともに、仮焼熱処理のうち少なくとも最外層の前駆体を除く仮焼熱処理温度を250～350℃の範囲内で、かつ結晶化熱処理中の少なくとも最外層の前駆体の結晶化到達前の結晶化熱処理雰囲気中の導入ガスの水蒸気分圧を0.5～3.2vol%の範囲内で行うことにより厚膜のテープ状酸化物超電導体を容易に得ることができる。

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【特許請求の範囲】

【請求項1】基板上に、酸化物超電導体を構成する各金属元素を所定のモル比で含む金属有機酸塩の混合溶液を塗布し、仮焼熱処理を施した酸化物超電導前駆体に結晶化熱処理を施した酸化物超電導体において、結晶化熱処理後の酸化物超電導体の厚さが0.5  $\mu\text{m}$ 以上で、77Kにおける臨界電流密度が0.7 MA/cm<sup>2</sup>を有することを特徴とする厚膜テープ状酸化物超電導体。

【請求項2】酸化物超電導前駆体は、その膜中に存在する結晶化した酸化物及びフッ化物の粒径が0.3  $\mu\text{m}$ 以下であることを特徴とする請求項1記載の厚膜テープ状酸化物超電導体。

【請求項3】酸化物超電導前駆体は、基板上に複数層形成されていることを特徴とする請求項1又は2記載の厚膜テープ状酸化物超電導体。

【請求項4】仮焼熱処理は、少なくとも最外層の酸化物超電導前駆体を除く仮焼熱処理温度が400℃未満で行われることを特徴とする請求項3記載の厚膜テープ状酸化物超電導体。

【請求項5】仮焼熱処理温度は、250～350℃であることを特徴とする請求項4記載の厚膜テープ状酸化物超電導体。

【請求項6】結晶化熱処理は、水蒸気分圧が4.0 vol %以下の雰囲気中で行われることを特徴とする請求項1乃至5いずれか1項記載の厚膜テープ状酸化物超電導体。

【請求項7】水蒸気分圧は、0.5～3.2 vol %の範囲であることを特徴とする請求項6項記載の厚膜テープ状酸化物超電導体。

【請求項8】少なくとも最外層の酸化物超電導前駆体の結晶化到達前の結晶化熱処理は、水蒸気分圧が0.5～3.2 vol %の雰囲気中で行われることを特徴とする請求項3乃至7いずれか1項記載の厚膜テープ状酸化物超電導体。

【請求項9】最外層の酸化物超電導前駆体の結晶化到達後の結晶化熱処理は、結晶化到達前の水蒸気分圧以下で行われることを特徴とする請求項3乃至8いずれか1項記載の厚膜テープ状酸化物超電導体。

【請求項10】結晶化熱処理は、水蒸気、酸化物超電導体と反応しないガス及び酸素からなる混合ガスを導入した雰囲気中で行われることを特徴とする請求項1乃至9いずれか1項記載の厚膜テープ状酸化物超電導体。

【請求項11】酸化物超電導体は、 $\text{RE}_{1-x}\text{Ba}_x\text{Cu}_2\text{O}_y$ （ここでREは、Y、Nd、Sm、Gd、Eu、Yb、Pr又はHoから選択された少なくとも1種以上の元素を示す。以下同じ。）からなることを特徴とする請求項1乃至10いずれか1項記載の厚膜テープ状酸化物超電導体。

【請求項12】金属有機酸塩は、トリフルオロ酢酸塩、オクチル酸塩、ナフテン酸塩又は酢酸塩のいずれか1種

以上からなることを特徴とする請求項1乃至11いずれか1項記載の厚膜テープ状酸化物超電導体。

【請求項13】金属有機酸塩は、少なくともトリフルオロ酢酸塩を含むことを特徴とする請求項1乃至12いずれか1項記載の厚膜テープ状酸化物超電導体。

【請求項14】 $\text{RE}_{1-x}\text{Ba}_x\text{Cu}_2\text{O}_y$ からなる酸化物超電導体を構成する各金属元素を所定のモル比で含む金属有機酸塩の混合溶液を基板上に塗布した後、仮焼熱処理を施すことにより酸化物超電導前駆体を形成し、次いで結晶化熱処理を施すことにより前記酸化物超電導前駆体を結晶化させて酸化物超電導体を製造する方法において、前記基板上に酸化物超電導前駆体を複数層形成するとともに、前記仮焼熱処理のうち少なくとも最外層の酸化物超電導前駆体を除く仮焼熱処理温度を400℃未満で行い、かつ前記結晶化熱処理雰囲気中の導入ガスの水蒸気分圧を4.0 vol %以下に行うことを特徴とする厚膜テープ状酸化物超電導体の製造方法。

【請求項15】仮焼熱処理温度が250～350℃の範囲で、かつ結晶化熱処理雰囲気中の導入ガスの水蒸気分圧が0.5～3.2 vol %の範囲であることを特徴とする請求項14記載の厚膜テープ状酸化物超電導体の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は酸化物超電導体及びその製造方法に係り、特に超電導マグネット、超電導ケーブル、電力機器等に適用可能な線材化に適する厚膜テープ状酸化物超電導体及びその製造方法に関する。

【0002】

【従来の技術】酸化物超電導体は、その臨界温度（ $T_c$ ）が液体窒素温度を超えることから超電導マグネット、超電導ケーブル及び電力機器等への応用が期待されており、種々の研究が鋭意進められている。

【0003】酸化物超電導体を上記の分野に適用するためには、臨界電流密度（ $J_c$ ）が高く、かつ長尺の線材を製造する必要があり、一方、長尺テープを得るためには、強度及び可撓性の観点から金属テープ上に酸化物超電導体を形成する必要がある。

【0004】また酸化物超電導体はその結晶学的方向により超電導特性が変化することから、面内配向性を向上させることが必要であり、このためにも酸化物超電導体をテープ状の基板上に形成する必要がある。この場合、臨界電流密度を向上させるため、酸化物超電導体のc軸を基板の板面に垂直に配向させ、かつそのa軸（又はb軸）をほぼ電流方向に平行に面内配向させて、超電導状態の量子的結合性を良好に保持する必要がある。

【0005】テープ状のRE系酸化物超電導体、即ち、 $\text{RE}_{1-x}\text{Ba}_x\text{Cu}_2\text{O}_y$ （ここでREは、Y、Nd、Sm、Gd、Eu、Yb、Pr又はHoから選択された少なくとも1種以上の元素を示す。以下同じ。）系

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酸化物超電導体の製造方法として、MOD法が知られている。

【0006】このMOD法(Metal Organic Deposition Processes:有機酸塩堆積法)は、金属有機酸塩を熱分解させるもので、金属成分の有機化合物を均一に溶解した溶液を基板上に塗布した後、これを加熱して熱分解させることにより基板上に薄膜を形成する方法であり、非真空プロセスで高いJcが得られる他、低コストで高速成膜が可能であるため長尺のテープ状の酸化物超電導体材料の製造に適する利点を有する。

【0007】MOD法においては、出発原料である金属有機酸塩を熱分解させると通常アルカリ土類金属(Ba等)の炭酸塩が生成されるが、この炭酸塩を経由する固相反応による酸化物超電導体の形成には800℃以上の高温熱処理を必要とする。そのため、フッ素を含む有機酸塩(例えば、TFA塩:トリフルオロ酢酸塩)を出発原料とし、水蒸気雰囲気中での熱処理及び水蒸気分圧の制御により、RE(123)超電導体(RE:Ba:Cu=1:2:3、以下同じ。)を形成する方法が近年精力的に行われている。

【0008】このTFA塩を出発原料とする方法は、溶液中に核生成を生ぜず、水蒸気とフッ素を含むアモルファス前駆体との反応により基板からRE(123)超電導体をエピタキシャル成長させることかできる。

【0009】

【発明が解決しようとする課題】上述のように、MOD法によりテープ状の酸化物超電導体を製造する場合、実用化のためには臨界電流値(Jc)を向上させるための厚膜化が必要不可欠である。この厚膜化をTFA塩を出発原料とするMOD法により達成するために、TFA塩を含む原料溶液の粘性を高くして塗布膜を厚くすることが考えられるが、1回で塗布する膜厚が厚くなると仮焼時に分解生成するHF及びCO<sub>2</sub>ガスの量が増加することにより、塗布膜が飛散する現象が生じ、結果として厚膜のテープ状酸化物超電導体を製造することはできない。

【0010】また、塗布及び仮焼の工程を繰返して塗布膜を厚くすることが考えられるが、この場合には、結晶化熱処理によって基板上に面内配向性に優れた超電導結晶を生成させることが困難となる。この理由は、結晶成長の核となる核生成が基板面以外の部分に生ずることによるものと考えられている。

【0011】本発明は、以上の問題点を解決するためになされたもので、基板上に形成した酸化物超電導前駆体の熱処理時の仮焼熱処理温度及び/又は結晶化熱処理雰囲気中の導入ガスの水蒸気分圧を制御することにより、高配向性と高Jc値を有する厚膜のテープ状酸化物超電導体及びその製造方法を提供することをその目的とする。

【0012】この酸化物超電導体の厚膜化は、1層又は

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多層構造の仮焼塗布膜の結晶化熱処理により達成することができる。

【0013】

【課題を解決するための手段】以上の目的を達成するために、本願請求項1に係る発明、即ち、厚膜テープ状酸化物超電導体は、基板上に酸化物超電導体を構成する各金属元素を所定のモル比で含む金属有機酸塩の混合溶液を塗布し、仮焼熱処理を施した酸化物超電導前駆体に結晶化熱処理を施した酸化物超電導体において、結晶化熱処理後の酸化物超電導体の厚さが0.5μm以上で、77Kにおける臨界電流密度が0.7MA/cm<sup>2</sup>を有するようにしたものである。

【0014】上記の酸化物超電導前駆体は、その膜中に存在する結晶化した酸化物及びフッ化物の粒径が0.3μm以下であるように制御することが結晶成長の点から好ましい。

【0015】また、上記の酸化物超電導前駆体を、基板上に複数層形成することにより厚膜化をより容易に達成することができる。

【0016】上記の仮焼熱処理は、少なくとも最外層の酸化物超電導前駆体を除く仮焼熱処理温度が400℃未満で行うことが好ましく、特に、仮焼熱処理温度が250～350℃の範囲であることが好ましい。

【0017】さらに、結晶化熱処理は、水蒸気分圧が4.0vol%以下の雰囲気中で行うことが好ましく、特に、水蒸気分圧が0.5～3.2vol%の範囲(更に好ましくは、水蒸気分圧が1.0～3.2vol%の範囲)にあることが好ましい。この場合、少なくとも最外層の酸化物超電導前駆体の結晶化到達前の結晶化熱処理雰囲気中の水蒸気分圧を0.5～3.2vol%の範囲(更に好ましくは、水蒸気分圧が1.0～3.2vol%の範囲)で行い、また、最外層の酸化物超電導前駆体の結晶化到達後の結晶化熱処理を、結晶化到達前の水蒸気分圧以下で行うことによりより優れた結果が得られる。

【0018】以上の結晶化熱処理は、水蒸気、酸化物超電導体と反応しないガス及び酸素からなる混合ガスを導入した雰囲気中で行われる。

【0019】酸化物超電導体は、金属有機酸塩の混合溶液を出発原料として形成されるが、この金属有機酸塩は、トリフルオロ酢酸塩、オクチル酸塩、ナフテン酸塩又は酢酸塩のいずれか一種以上からなることが好ましく、特に、少なくともトリフルオロ酢酸塩を含むことがより好ましい。

【0020】以上述べた酸化物超電導体は、本願請求項14に係る発明、即ち、RE<sub>x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>y</sub>からなる酸化物超電導体を構成する各金属元素を所定のモル比で含む金属有機酸塩の混合溶液を基板上に塗布した後、仮焼熱処理を施すことにより酸化物超電導前駆体を形成し、次いで結晶化熱処理を施すことにより酸化物超

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電導前駆体を結晶化させて酸化物超電導体を製造する方法において、基板上に酸化物超電導前駆体を複数層形成するとともに、仮焼熱処理のうち少なくとも最外層の酸化物超電導前駆体を除く仮焼熱処理温度を400℃未満で行い、かつ結晶化熱処理雰囲気中の導入ガスの水蒸気分圧を4.0vol%以下にして行うことにより製造することができる。

【0021】この場合、仮焼熱処理温度が250～350℃の範囲で、かつ結晶化熱処理雰囲気中の導入ガスの水蒸気分圧が0.5～3.2vol%の範囲であることが好ましく、特に、水蒸気分圧が1.0～3.2vol%の範囲であることが好ましい。

【0022】

【発明の実施の形態】本発明において使用される基板としては、単結晶基板又は多結晶基板のいずれも用いることができる。

【0023】単結晶基板としては $\text{LaAlO}_3$ （100）単結晶基板（以下、 $\text{LaO}$ 単結晶基板という。）等を用いることができ、一方、多結晶基板としては配向性 $\text{Ni}$ 基板や $\text{IBAD}$ 法（Ion Beam Assisted Deposition）を用いた複合基板等を用いることができる。

【0024】配向性 $\text{Ni}$ 基板は、冷間加工した $\text{Ni}$ 基板を真空中で熱処理を施して高配向させたもので、米国オークリッジ国立研究所で開発され、 $\text{RABiTS}$ （商標：rolling-assisted biaxially textured-substrate）と称されている。この配向性 $\text{Ni}$ 基板の上に、高温の不活性ガス雰囲気中でエレクトロンビーム蒸発によりセリウムを堆積させ、この堆積中に水蒸気を存在させることにより、 $\text{CeO}_2$ のエピタキシャル層の薄膜を設け、さらにその上にスパッタリング法により高温減圧下で $\text{YSZ}$ （イットリウム安定化ジルコニア）の厚膜を形成したものを基板として用いることができる。この $\text{CeO}_2$ 層及び $\text{YSZ}$ 層はバッファ層としての機能を有し、超電導層との反応を抑制して超電導特性の低下を防止し、超電導層との整合性を維持するために配置されている。さらに、上記の $\text{YSZ}$ 層の上に $\text{Y}_{1-x}\text{Ba}_x\text{Cu}_2\text{O}_7$ 超電導体（以下、 $\text{YBCO}$ という。）との結晶学的整合性により優れた $\text{CeO}_2$ の薄膜を設けたものも基板として用いることができる。

【0025】さらに、 $\text{IBAD}$ 法を用いた複合基板（以下、 $\text{IBAD}$ 複合基板という。）は、非磁性で高強度のテープ状 $\text{Ni}$ 系基板上（ハステロイ等）に、この $\text{Ni}$ 系基板に対して斜め方向からイオンを照射しながら、ターゲットから発生した粒子を堆積させて形成した高配向性を有し超電導体を構成する元素との反応を抑制する中間層（ $\text{CeO}_2$ 、 $\text{Y}_2\text{O}_3$ 、 $\text{YSZ}$ 等）を設けたもので、上記の中間層を2層構造としたもの（ $\text{YSZ}$ 又は $\text{ZrO}_2$ ／ $\text{CeO}_2$ 又は $\text{Y}_2\text{O}_3$ 等； $\text{Rxt}$ は、 $\text{Y}$ 、 $\text{Nd}$ 、 $\text{Sm}$ 、 $\text{Gd}$ 、 $\text{Er}$ 、 $\text{Yb}$ 、 $\text{Ho}$ 、 $\text{Tm}$ 、 $\text{Dy}$ 、 $\text{Ce}$ 、 $\text{La}$ 又は $\text{Er}$ を示す。）もよく適合する（特開平4-329867号、特開平4

-331795号、特開2000-333843号）。

【0026】本願発明においては、例えば、基板上に酸化物超電導前駆体を複数層形成するとともに、仮焼熱処理のうち少なくとも最外層の酸化物超電導前駆体を除く仮焼熱処理温度を400℃未満で行うことにより、厚膜の形成を可能とするものであるが、これは、例えば、3層構造の仮焼膜を結晶化させて酸化物超電導体を形成する場合、1及び2層目の仮焼熱処理温度を400℃未満、好ましくは250～350℃の温度範囲で行うことを意味しており、3層目の仮焼熱処理温度は400℃未満でも400℃を越えても問題はない。

【0027】また、本願発明においては、例えば、結晶化熱処理雰囲気中の導入ガスの水蒸気分圧を4.0vol%以下にして行うものであるが、この場合には前駆体の複数層形成に加えて高粘度の溶液を用いて1層の仮焼膜の結晶化によっても厚膜化が可能になる。

【0028】本願発明においては、例えば、基板上に酸化物超電導前駆体を複数層形成するとともに、結晶化熱処理中の少なくとも最外層の酸化物超電導前駆体の結晶化到達前の結晶化熱処理雰囲気中の導入ガスの水蒸気分圧を4.0vol%以下にして行うものであるが、これは、例えば、3層構造の仮焼膜を結晶化させて酸化物超電導体を形成する場合、3層目の結晶化が開始されるまでの1及び2層目の結晶化熱処理中の導入ガスの水蒸気分圧を4.0vol%以下、好ましくは0.5～3.2vol%の範囲（更に好ましくは、1.0～3.2vol%の範囲）で行うことを意味しており、結晶化熱処理雰囲気中の導入ガスは、水蒸気、酸化物超電導体と反応しないガス及び酸素からなる混合ガスが用いられ、結晶化熱処理雰囲気中の導入ガスの水蒸気分圧は、以上の条件が満足されれば、一定の勾配下又は段階的に上昇させることもできる。

【0029】また、最外層の酸化物超電導前駆体の結晶化到達後の結晶化熱処理は、結晶化到達前の水蒸気分圧以下で行われることが好ましいが、特に、結晶化終了後は水蒸気と超電導体との反応による特性の劣化を抑制するために乾燥ガスを導入することが好ましい。

【0030】

【実施例】実施例1

基板として、長さ10mm、幅10mm、厚さ0.5mmの $\text{LaO}$ 単結晶基板を用いた。

【0031】この基板上に各金属 $\text{TFA}$ 塩を $\text{Y}:\text{Ba}:\text{Cu}$ のモル比が1:2:3となるようにメタノールに溶解し、溶液濃度を $\text{Y}$ 換算で0.25mol／リットルに調整して原料溶液を作成した。

【0032】この原料溶液を基板上にスピコート法により塗布して塗布膜を形成した。このようにして得られた基板上の塗布膜に対して、水蒸気を含んだ酸素雰囲気下で低昇温速度で300℃まで加熱した後炉冷し、次いで再度上記と同様の方法により原料溶液をさらに塗布し

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て塗布膜を形成した後、水蒸気を含んだ酸素雰囲気下で低昇温速度で400℃まで加熱し、次いで炉冷してY-Ba-Cu前駆体を得た。

【0033】この仮焼熱処理に続く結晶化熱処理においては、上記の前駆体膜を水蒸気を含んだ10<sup>-1</sup> atmの低酸素雰囲気下で25℃/minの昇温速度で加熱し、基板温度を750℃に維持して結晶化熱処理後、次いで炉内雰囲気を乾燥ガスに切替えて10分間保持した後、炉冷した。

【0034】以上の場合において、水蒸気は導入ガスを30℃の脱イオン水の入ったフラスコ中をバブリングさせることにより炉内に導入した。また、1回の塗布で得られる超電導体の膜厚は約0.2μmである。

\*

	実施例 1	比較例 1	
基板	LAO 単結晶基板		
塗布回数 (回)	2	1	2
膜厚 (μm)	0.4	0.2	0.4
仮焼温度 (1回目 : °C)	300	400	400
仮焼温度 (2回目 : °C)	400	—	400
c 軸配向率 (%)	80	95	50
a 軸配向率 (%)	20	5	50
Tc (K)	92	92	86

#### 【0039】比較例1

実施例1と同様の方法によりLAO単結晶基板を用いて、原料溶液を基板上に塗布して塗布膜を形成した。このようにして得られた基板上の塗布膜に対して、水蒸気を含んだ酸素雰囲気下で低昇温速度で400℃まで加熱した後、炉冷してY-Ba-Cu前駆体を得た(塗布回数1)。さらに、別途再度この仮焼膜上に上記と同様の方法により原料溶液を塗布して塗布膜を形成した後、水蒸気を含んだ酸素雰囲気下で低昇温速度で400℃まで加熱した後炉冷してY-Ba-Cu前駆体を得た(塗布回数2)。これらの2種類のY-Ba-Cu前駆体に対して以後実施例1と同様の方法により、超電導体をLAO単結晶基板上に形成した。

【0040】この超電導膜はX線回折の結果、いずれもYBCOが主成分であることが確認された。

【0041】この超電導膜について、実施例1と同様にTc、c軸及びa軸配向率を測定した。結果を表1に同時に示した。

\*【0035】以上のようにして得られた膜上に銀を蒸着して電極を形成し、酸素雰囲気中で450℃で1時間熱処理を施して超電導膜を形成した。

【0036】この超電導膜はX線回折の結果、YBCOが主成分であることが確認された。

【0037】この超電導膜について、直流4端子法によりTcを測定した。またYBCO(102)極点図により、c軸及びa軸配向率を測定した。LAO単結晶基板を用いた場合のTc及びc軸及びa軸配向率の測定結果を表1に示す。

【0038】

【表1】

#### 【0042】実施例2

基板としてハステロイ/YSZ/CeO<sub>2</sub>からなるIBAD複合基板を用いた。この複合基板は、約10nmの平均結晶粒を有し、長さ10mm、幅10mm、厚さ0.1mmのハステロイテープ上に、IBAD法を用いて室温下でYSZの第1中間層を1μmの厚さに成膜し、この上にスパッタリング法を用いてCeO<sub>2</sub>の第2中間層を厚さ0.5μmに形成して作成した。

【0043】この複合基板を用いた以外は実施例1と同様の方法により、超電導体を複合基板上に形成した。この超電導膜はX線回折の結果、YBCOが主成分であることが確認された。

【0044】この超電導膜について、実施例1と同様にTc、c軸及びa軸配向率を測定した。結果を表2に示す。

【0045】

【表2】

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	実施例2	比較例2	
基板	I B A D 複合基板		
塗布回数 (回)	2	1	2
膜厚 (μm)	0.4	0.2	0.4
仮焼温度 (1回目:℃)	300	400	400
仮焼温度 (2回目:℃)	400	—	400
c 軸配向率 (%)	74	90	40
a 軸配向率 (%)	26	10	60
Tc (K)	92	92	84

## 【0046】比較例2

基板として、実施例2のハステロイ/YSZ/ $\text{CeO}_2$ からなるI B A D 複合基板を用いた以外は比較例1と同様の方法により、2種類の超電導体をI B A D 複合基板上に形成した。この超電導膜はX線回折の結果、Y B C O が主成分であることが確認された。

【0047】この超電導膜について、実施例1と同様にしてTc、c 軸及びa 軸配向率を測定した。結果を表2に示した。

【0048】以上の実施例1及び2並びに比較例1及び2の結果から明らかなように、仮焼膜を2層に形成した場合、1層目の仮焼熱処理を300 $^{\circ}\text{C}$ で行った場合を400 $^{\circ}\text{C}$ で行った場合と比較すると、いずれの基板を用いた場合でも、Tcが向上するとともに、c 軸配向率が著しく向上していることが認められる。これらの値は仮焼膜を1層に形成した場合と比較して、c 軸配向率は低下するものの、Tcは同等のレベルにあることを示している。

【0049】仮焼膜を1層又は2層に形成し、仮焼熱処理を400 $^{\circ}\text{C}$ で行った場合には、2層の仮焼膜は1層の仮焼膜に対してTcは92Kから84~86Kへと低下するとともにc 軸配向率も著しく低下する。

【0050】この原因は、結晶化熱処理時の1層目と2層目の界面の不純物層の生成により、基板からのエピタキシャル成長を妨げることによるものと考えられる。この不純物層の生成の要因としては、仮焼熱処理温度が高い場合にアモルファス前駆体膜中の結晶化が進行し、結\*

\* 結晶化熱処理時に1層目と2層目の仮焼膜とその結晶粒が優先的に反応し不純物が生成し易くなるものと考えられる。

【0051】また、以上の実施例1及び2の結果から、1層目の仮焼熱処理を低くして仮焼膜を2層に形成した場合には、基板として単結晶を用いた場合とI B A D 複合基板を用いた場合との間でTc及びc 軸配向率に差は殆ど認められない。さらに比較例1及び2の結果から、仮焼膜を1層に形成した場合のTc及びc 軸配向率の基板による差も殆ど認められない。

## 【0052】実施例3

結晶化熱処理雰囲気中の導入ガスの水蒸気分圧(1.05vol%)と結晶化熱処理時間を変えた他は、実施例1と同様の方法により300 $^{\circ}\text{C}$ で仮焼し、さらに400 $^{\circ}\text{C}$ で仮焼してL A O 単結晶基板上に仮焼膜を1層又は2層に形成し、次いで結晶化熱処理を施して超電導膜を形成した。また、300 $^{\circ}\text{C}$ で4層まで仮焼し5層目を400 $^{\circ}\text{C}$ で仮焼した例も同時に示した。この超電導膜はX線回折の結果、Y B C O が主成分であることが確認された。

【0053】この超電導膜のJc値及びIc値(電圧基準1 $\mu\text{V}/\text{cm}$ )を、直流4端子法により測定した。またX線回折(ロッキングカーブ)により、Y B C O (005)面に対応するピークの積分強度及び半値幅を求めた。結果を表3に示す。

## 【0054】

【表3】

	実施例3		比較例3			
基板			L A O 単結晶基板			
水蒸気分圧 (vol%)	1.05	1.05	1.05	4.2	4.2	4.2
熱処理時間 (min)	60	180	300	60	60	120
塗布回数 (回)	1	2	5	1	2	5
膜厚 ( $\mu\text{m}$ )	0.2	0.4	1.0	0.2	0.4	1.0
Jc (MA/cm <sup>2</sup> )	4	8	2	3.7	1.3	0.4
Ic (A)	80	120	200	74	52	40
ピーク積分強度	11448	18256	32628	9714	11574	15238
半値幅 (deg.)	0.33	0.57	0.62	0.38	0.71	0.95

(Jc: 77K)

## 【0055】比較例3

結晶化熱処理雰囲気中の導入ガスの水蒸気分圧(4.2vol%)と熱処理時間を変えた他は、実施例1と同様

の方法により300 $^{\circ}\text{C}$ で仮焼し、さらに400 $^{\circ}\text{C}$ で仮焼してL A O 単結晶基板上に仮焼膜を1層、2層又は5層に形成し、次いで結晶化熱処理を施して超電導膜を形成



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した。この超電導膜はX線回折の結果、YBCOが主成分であることが確認された。

【0056】この超電導膜のJc値、Ic値、ピーク積分強度及び半値幅を実施例3と同様にして測定した。結果を表3に示した。

【0057】以上の実施例3及び比較例3の結果から明らかなように、仮焼膜を1層に形成し、水蒸気分圧を1.05vol%又は4.2vol%に変化させた場合には、Jc値及びIc値は多少変化するもののその差は小さい。

【0058】また、仮焼膜を2層に形成し、水蒸気分圧を1.05vol%と低下させて結晶化熱処理を施した場合に、仮焼膜を1層に形成した場合と比較して、Jc値は多少低下するもののIc値は1.5倍程度増加する。

【0059】これに対して、仮焼膜を2層に形成し、水蒸気分圧を4.2vol%で結晶化熱処理を施した場合には、仮焼膜を1層に形成した場合と比較して、Jc値は著しく低下する上、Ic値も低下する結果を示しており、この場合のロッキングカーブからYBCOのc軸配\*20

\*向率の低下が確認された。

【0060】以上の結果は、結晶化熱処理時の水蒸気分圧が増加するとYBCO膜の結晶の成長速度が大きくなるため、結晶性及びc軸配向率が低下することによるものと考えられる。

【0061】実施例4

溶液濃度を0.63mol/リットルに調整した高濃度の原料溶液により1回の塗布で厚膜を形成し、結晶化熱処理雰囲気中の導入ガスの水蒸気分圧(1.05vol%)と熱処理時間を変えた他は、実施例1と同様の方法により400℃で仮焼してLAO単結晶基板上に厚膜の仮焼膜を1層形成し、次いで結晶化熱処理を施して超電導膜を形成した。この超電導膜はX線回折の結果、YBCOが主成分であることが確認された。

【0062】この超電導膜のJc値、Ic値、ピーク積分強度及び半値幅を実施例3と同様にして測定した。結果を表4に示す。

【0063】

【表4】

	実施例4	比較例4
基板	LAO単結晶基板	
水蒸気分圧(vol%)	1.05	4.2
熱処理時間(min)	180	60
塗布回数(回)	1	1
膜厚(μm)	0.5	0.5
Jc(MA/cm <sup>2</sup> )	2.4	0.6
Ic(A)	120	30
ピーク積分強度	20134	9876
半値幅(deg.)	0.6	0.82

(Jc:77K)

【0064】比較例4

溶液濃度を0.63mol/リットルに調整した高濃度の原料溶液により1回の塗布で厚膜を形成し、結晶化熱処理雰囲気中の導入ガスの水蒸気分圧(4.2vol%)と熱処理時間を変えた他は、実施例1と同様の方法により400℃で仮焼してLAO単結晶基板上に仮焼膜を1層形成し、次いで結晶化熱処理を施して超電導膜を形成した。この超電導膜はX線回折の結果、YBCOが主成分であることが確認された。

【0065】この超電導膜のJc値、Ic値、ピーク積分強度及び半値幅を実施例3と同様にして測定した。結果を表4に示した。

【0066】以上の実施例4及び比較例4の結果から明らかなように、原料溶液の濃度を大きくして厚膜(0.5μm)の仮焼膜を1層に形成し、水蒸気分圧を1.05vol%と低下させて結晶化熱処理を施した場合には、仮焼膜を0.2μmの厚さの1層に形成した場合と比較して(実施例3参照)、Jc値は約60%程度に低下するもののIc値は1.5倍程度増加する。

【0067】これに対して、原料溶液の濃度を大きくし

て厚膜(0.5μm)の仮焼膜を1層に形成し、水蒸気分圧を4.2vol%で結晶化熱処理を施した場合には、仮焼膜を0.2μmの厚さの1層に形成した場合と比較して(比較例3参照)、Jc値及びIc値も大きく低下する結果を示しており、この場合のロッキングカーブからYBCOのc軸配向率の低下が確認された。

【0068】この理由も結晶化熱処理時の水蒸気分圧が増加すると、YBCO膜の結晶の成長速度が大きくなり、結晶性及びc軸配向率が低下するためと考えられる。

【0069】実施例5

実施例3のLAO単結晶基板に代えて実施例2のハステロイ/YSZ/CeO<sub>2</sub>からなるIBAD複合基板を用いた他は実施例3と同様の方法により、この複合基板上に仮焼膜を1層又は2層に形成し、次いで結晶化熱処理を施して超電導膜を形成した。この超電導膜はX線回折の結果、YBCOが主成分であることが確認された。

【0070】この超電導膜のJc値、Ic値、ピーク積分強度及び半値幅を実施例3と同様にして測定した。結果を表5に示す。

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[0071]

\* \* [表5]

	実施例5		比較例5	
基板	IBAD複合基板			
水蒸気分圧(vol%)	1.05	1.05	4.2	4.2
熱処理時間(min)	60	180	60	60
塗布回数(回)	1	2	1	2
膜厚(μm)	0.2	0.4	0.2	0.4
Jc(MA/cm <sup>2</sup> )	3	2.3	2.4	0.7
Ic(A)	60	90	48	28
ピーク積分強度	8586	13693	6301	7507
半値幅(deg.)	0.33	0.60	0.45	1.10

(Jc: 77K)

[0072] 比較例5

実施例3のLAO単結晶基板に代えて実施例2のハステロイ/YSZ/CeO<sub>2</sub>からなるIBAD複合基板を用いた他は比較例3と同様の方法により、この複合基板上に仮焼膜を1層又は2層に形成し、次いで結晶化熱処理を施して超電導膜を形成した。この超電導膜はX線回折の結果、YBCOが主成分であることが確認された。

[0073] この超電導膜のJc値、Ic値、ピーク積分強度及び半値幅を実施例3と同様にして測定した。結果を表5に示した。

[0074] 実施例6

※実施例3のLAO単結晶基板に代えて実施例2のハステロイ/YSZ/CeO<sub>2</sub>からなるIBAD複合基板を用いた他は実施例4と同様の方法により、高濃度の原料溶液を用いて1回の塗布で厚膜を形成し、結晶化熱処理を施して超電導膜を形成した。この超電導膜はX線回折の結果、YBCOが主成分であることが確認された。

[0075] この超電導膜のJc値、Ic値、ピーク積分強度及び半値幅を実施例3と同様にして測定した。結果を表6に示す。

[0076]

\* [表6]

	実施例6	比較例6
基板	IBAD複合基板	
水蒸気分圧(vol%)	1.05	4.2
熱処理時間(min)	180	60
塗布回数(回)	1	1
膜厚( $\mu\text{m}$ )	0.5	0.5
$J_c$ (MA/cm <sup>2</sup> )	1.8	0.5
$I_c$ (A)	90	25
ピーク積分強度	15432	6937
半値幅(deg.)	0.65	1.3

(Jc: 77K)

[0077] 比較例6

実施例3のLAO単結晶基板に代えて実施例2のハステロイ/YSZ/CeO<sub>2</sub>からなるIBAD複合基板を用いた他は比較例4と同様の方法により、高濃度の原料溶液を用いて1回の塗布で厚膜を形成し、結晶化熱処理を施して超電導膜を形成した。この超電導膜はX線回折の結果、YBCOが主成分であることが確認された。

[0078] この超電導膜のJc値、Ic値、ピーク積分強度及び半値幅を実施例3と同様にして測定した。結果を表6に示した。

[0079] 以上の複合基板を用いた実施例5及び6並びに比較例5及び6の結果は、それぞれLAO単結晶基板を用いた実施例3及び4並びに比較例3及び4と比較して、Jc値及びIc値は低下するものの同様の傾向を

示す結果が得られた。

[0080]

【発明の効果】以上述べたように、本発明によれば、基板上に形成した酸化物超電導前駆体の熱処理時の仮焼熱処理温度及び/又は結晶化熱処理雰囲気中の導入ガスの水蒸気分圧を制御することにより、高配向性かつ高Jc値を有する厚膜のテープ状酸化物超電導体が得られる。また、この酸化物超電導体の厚膜化は1層又は多層構造の仮焼塗布膜の結晶化熱処理により達成することができる。とともに、非真空プロセスであるMOD法により超電導層を形成するため、長尺継手に適し、その製造コストを著しく低減させることができ、超電導マグネットや超電導ケーブルへの応用に適する。

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CLAIMS

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[Claim(s)]

[Claim 1] Thick-film tape-like oxides superconductors characterized by critical current density [ in / in the thickness of the oxides superconductors after heat-of-crystallization processing / 77K ] having 0.7 MA/cm<sup>2</sup> by 0.5 micrometers or more in the oxides superconductors which performed heat-of-crystallization processing to the oxide superconductivity precursor which applied on the substrate the mixed solution of the metal organic-acid salt which contains each metallic element which constitutes oxides superconductors by the predetermined mole ratio, and performed temporary-quenching heat treatment.

[Claim 2] Oxide superconductivity precursors are thick-film tape-like oxides superconductors according to claim 1 characterized by the particle size of the crystallized oxide which exists in the film, and a fluoride being 0.3 micrometers or less.

[Claim 3] Oxide superconductivity precursors are thick-film tape-like oxides superconductors according to claim 1 or 2 characterized by forming two or more layers on a substrate.

[Claim 4] For temporary-quenching heat treatment, the temporary-quenching heat treatment temperature except the oxide superconductivity precursor of the outermost layer is the thick-film tape-like oxides superconductors according to claim 3 characterized by being carried out at less than 400 degrees C at least.

[Claim 5] Temporary-quenching heat treatment temperature is thick-film tape-like oxides superconductors according to claim 4 characterized by being 250-350 degrees C.

[Claim 6] For heat-of-crystallization processing, a steam partial pressure is claim 1 characterized by being carried out in the ambient atmosphere not more than 4.0vol% thru/or thick-film tape-like oxides superconductors given in 5 any 1 terms.

[Claim 7] Steam partial pressures are thick-film tape-like oxides superconductors given in claim 6 term characterized by being the range of 0.5 - 3.2vol%.

[Claim 8] The heat-of-crystallization processing at least before crystallization attainment of the oxide superconductivity precursor of the outermost layer is claim 3 characterized by being carried out in the ambient atmosphere whose steam partial pressure is 0.5 - 3.2vol% thru/or thick-film tape-like oxides superconductors given in 7 any 1 terms.

[Claim 9] The heat-of-crystallization processing after crystallization attainment of the oxide superconductivity precursor of the outermost layer is claim 3 characterized by being carried out by being below a steam partial pressure before crystallization attainment thru/or thick-film tape-like oxides superconductors given in 8 any 1 terms.

[Claim 10] Heat-of-crystallization processing is claim 1 characterized by being carried out in the ambient atmosphere which introduced the mixed gas which consists of the gas and oxygen which do not react with a steam and oxides superconductors thru/or thick-film tape-like oxides superconductors given in 9 any 1 terms.

[Claim 11] Oxides superconductors are RE<sub>1</sub>+X Ba<sub>2</sub>-X Cu<sub>3</sub> O<sub>Y</sub> (RE shows at least one or more sorts of elements chosen from Y, Nd, Sm, Gd, Eu, Yb, Pr, or Ho here.). below the same. from -- claim 1

characterized by becoming thru/or thick-film tape-like oxides superconductors given in 10 any 1 terms.

[Claim 12] A metal organic-acid salt is claim 1 characterized by consisting of any one or more sorts of a trifluoroacetic acid salt, an octylic acid salt, naphthenate, or acetate thru/or thick-film tape-like oxides superconductors given in 11 any 1 terms.

[Claim 13] A metal organic-acid salt is claim 1 characterized by including a trifluoroacetic acid salt at least thru/or thick-film tape-like oxides superconductors given in 12 any 1 terms.

[Claim 14]  $RE1+X Ba2-X Cu3 OY$  from, after applying the mixed solution of the metal organic-acid salt which contains each metallic element which constitutes the becoming oxides superconductors by the predetermined mole ratio on a substrate In the approach of forming an oxide superconductivity precursor, crystallizing said oxide superconductivity precursor by subsequently performing heat-of-crystallization processing, and manufacturing oxides superconductors by performing temporary-quenching heat treatment While forming a two or more layers oxide superconductivity precursor on said substrate, temporary-quenching heat treatment temperature except the oxide superconductivity precursor of the outermost layer is performed at less than 400 degrees C at least among said temporary-quenching heat treatments. And the manufacture approach of the thick-film tape-like oxides superconductors characterized by making the steam partial pressure of the introductory gas in said heat-of-crystallization processing ambient atmosphere into less than [ 4.0vol% ], and performing it.

[Claim 15] The manufacture approach of the thick-film tape-like oxides superconductors according to claim 14 characterized by being the range whose temporary-quenching heat treatment temperature is 250-350 degrees C, and being the range whose steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere is 0.5 - 3.2vol%.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the thick-film tape-like oxides superconductors which are built over an oxide superconductivity object and its manufacture approach, especially are suitable for wire rod-ization applicable to a superconduction magnet, a superconduction cable, a power device, etc., and its manufacture approach.

[0002]

[Description of the Prior Art] Since, as for oxides superconductors, the critical temperature ( $T_c$ ) exceeds liquid nitrogen temperature, the application to a superconduction magnet, a superconduction cable, a power device, etc. is expected, and various researches are advanced wholeheartedly.

[0003] In order to apply oxide super-\*\*\*\* to the above-mentioned field, critical current density ( $J_c$ ) is high, and it is necessary to manufacture a long wire rod, and on the other hand, in order to obtain a long tape, it is necessary to form oxide super-\*\*\*\* on a metal tape from reinforcement and a flexible viewpoint.

[0004] Moreover, since a superconduction property changes with those crystallographic directions, oxides superconductors need to raise the stacking tendency within a field, and, also for this reason, need to form oxides superconductors on a tape-like substrate. In this case, in order to raise critical current density, it is necessary to carry out orientation of the c-axis of oxides superconductors at right angles to the plate surface of a substrate, and to carry out orientation within a field of that a-axis (or b-axis) almost in parallel with the direction of a current, and to hold the quantum affinity of a superconducting state good.

[0005] (Tape-like RE system oxides superconductors (RE shows at least one or more sorts of elements chosen from Y, Nd, Sm, Gd, Eu, Yb, Pr, or Ho here.), i.e.,  $RE1+X Ba2-X Cu3 OY$ ) It is below the same. The MOD method is learned as the manufacture approach of system oxides superconductors.

[0006] This MOD method (Metal Organic Deposition Processes: the organic-acid salt depositing method) After applying on a substrate the solution which is made to carry out the pyrolysis of the metal organic-acid salt, and dissolved the organic compound of a metal component in homogeneity, It is the approach of forming a thin film on a substrate by heating and carrying out the pyrolysis of this, high  $J_c$  is obtained in a gassiness process, and also by low cost, since high-speed membrane formation is possible, it has an advantage suitable for manufacture of the oxide superconductivity wire rod of the shape of a long tape.

[0007] In the MOD method, although the carbonate of alkaline earth metal (Ba etc.) will usually be generated if the pyrolysis of the metal organic-acid salt which is a start raw material is carried out, elevated-temperature heat treatment of 800 degrees C or more is needed for formation of the oxides superconductors by the solid phase reaction which goes via this carbonate. Therefore, the organic-acid salt (for example, a TFA salt: trifluoroacetic acid salt) containing a fluorine is used as a start raw material, and the approach of forming RE (123) superconductor (it being the same RE:Ba:Cu=1:2:3 and the following.) by heat treatment in a steam ambient atmosphere and control of a steam partial pressure

is performed energetically in recent years.

[0008] The approach of using this TFA salt as a start raw material can be done [ not producing a nucleation in a solution but carrying out epitaxial growth of the RE (123) superconductor from a substrate by the reaction of a steam and the amorphous precursor containing a fluorine, or ].

[0009]

[Problem(s) to be Solved by the Invention] As mentioned above, when manufacturing tape-like oxides superconductors by the MOD method, for utilization, thick-film-izing for raising a critical current value ( $I_c$ ) is indispensable. Although it is possible to make high viscosity of the raw material solution containing a TFA salt, and to thicken the spreading film in order to attain this thick-film-ization for a TFA salt by the MOD method used as a start raw material HF and CO<sub>2</sub> which will carry out decomposition generation at the time of temporary quenching if the thickness applied at once becomes thick When the amount of gas increases, the phenomenon in which the spreading film disperses arises and the tape-like oxides superconductors of a thick film cannot be manufactured as a result.

[0010] Moreover, although it is possible to repeat the process of spreading and temporary quenching and to thicken the spreading film, it becomes difficult by heat-of-crystallization processing to make the superconduction crystal excellent in the stacking tendency within a field generate on a substrate in this case. It is thought that it is because the nucleation used as the nucleus of crystal growth produces this reason into parts other than a substrate side.

[0011] This invention sets it as the purpose to offer the tape-like oxides superconductors and its manufacture approach of the thick film which has the tropism of your kind consideration, and a high  $J_c$  value by having been made in order to solve the above trouble, and controlling the temporary-quenching heat treatment temperature at the time of heat treatment of the oxide superconductivity precursor formed on the substrate, and/or the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere.

[0012] Heat-of-crystallization processing of one layer or the temporary-quenching spreading film of multilayer structure can attain thick-film-ization of these oxides superconductors.

[0013]

[Means for Solving the Problem] In order to attain the above purpose, invention concerning this application claim 1, i.e., thick-film tape-like oxides superconductors In the oxides superconductors which performed heat-of-crystallization processing to the oxide superconductivity precursor which applied on the substrate the mixed solution of the metal organic-acid salt which contains each metallic element which constitutes oxides superconductors by the predetermined mole ratio, and performed temporary-quenching heat treatment It is made for critical current density [ in / in the thickness of the oxides superconductors after heat-of-crystallization processing / 77K ] to have 0.7 MA/cm<sup>2</sup> by 0.5 micrometers or more.

[0014] As for the above-mentioned oxide superconductivity precursor, it is desirable from the point of crystal growth to control so that the particle size of the crystallized oxide which exists in the film, and a fluoride is 0.3 micrometers or less.

[0015] Moreover, thick-film-ization can be more easily attained by forming the two or more layers above-mentioned oxide superconductivity precursor on a substrate.

[0016] It is desirable that the temporary-quenching heat treatment temperature except the oxide superconductivity precursor of the outermost layer performs the above-mentioned temporary-quenching heat treatment at less than 400 degrees C at least, and it is desirable especially that it is the range whose temporary-quenching heat treatment temperature is 250-350 degrees C.

[0017] Furthermore, it is desirable that a steam partial pressure performs heat-of-crystallization processing in the ambient atmosphere not more than 4.0vol%, and it is desirable that it is in the range (range whose steam partial pressure is 1.0 - 3.2vol% still more preferably) whose steam partial pressure is 0.5 - 3.2vol% especially. In this case, the result of having excelled more for performing the steam partial pressure in the heat-of-crystallization processing ambient atmosphere before crystallization attainment of the oxide superconductivity precursor of the outermost layer at least in 0.5 - 3.2vol% (range whose steam partial pressure is 1.0 - 3.2vol% still more preferably), and being below a steam

partial pressure before crystallization attainment, and performing heat-of-crystallization processing after crystallization attainment of the oxide superconductivity precursor of the outermost layer is obtained. [0018] The above heat-of-crystallization processing is performed in the ambient atmosphere which introduced the mixed gas which consists of the gas and oxygen which do not react with a steam and oxides superconductors.

[0019] Although oxides superconductors are formed considering the mixed solution of a metal organic-acid salt as a start raw material, as for this metal organic-acid salt, it is desirable to consist of any one or more sorts of a trifluoroacetic acid salt, an octylic acid salt, naphthenate, or acetate, and it is more desirable that a trifluoroacetic acid salt is included especially at least.

[0020] invention which the oxides superconductors described above require for this application claim 14, i.e.,  $RE1+X Ba2-X Cu3 OY$ , from, after applying the mixed solution of the metal organic-acid salt which contains each metallic element which constitutes the becoming oxides superconductors by the predetermined mole ratio on a substrate In the approach of forming an oxide superconductivity precursor, crystallizing an oxide superconductivity precursor by subsequently performing heat-of-crystallization processing, and manufacturing oxides superconductors by performing temporary-quenching heat treatment While forming a two or more layers oxide superconductivity precursor on a substrate, temporary-quenching heat treatment temperature except the oxide superconductivity precursor of the outermost layer is performed at less than 400 degrees C at least among temporary-quenching heat treatments. And it can manufacture by making the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere into less than [ 4.0vol% ], and performing it.

[0021] In this case, it is desirable that it is the range whose temporary-quenching heat treatment temperature is 250-350 degrees C, and is the range whose steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere is 0.5 - 3.2vol%, and it is desirable especially that it is the range whose steam partial pressure is 1.0 - 3.2vol%.

[0022]

[Embodiment of the Invention] As a substrate used in this invention, either a single crystal substrate or a polycrystal substrate can be used.

[0023] as a single crystal substrate -- a  $LaAlO_3$  single-crystal (100) substrate (henceforth a LAO single crystal substrate) etc. -- it can use -- on the other hand -- as a polycrystal substrate -- a stacking tendency nickel substrate and IBAD -- the compound substrate using law (Ion Beam Assisted Deposition) etc. can be used.

[0024] A stacking tendency nickel substrate heat-treats and carries out high orientation of the nickel substrate which carried out cold working in a vacuum, is developed in U.S. Oak Ridge National Laboratory, and is called RABiTS (trademark: rolling-assisted biaxially textured-substrates). It is  $CeO_2$  by making a cerium deposit by EB evaporation in a hot inert gas ambient atmosphere on this stacking tendency nickel substrate, and making a steam exist during this deposition. The thin film of an epitaxial layer can be prepared and what formed the thick film of YSZ (yttrium fully stabilized zirconia) under elevated-temperature reduced pressure by the sputtering method on it further can be used as a substrate. This  $CeO_2$  A layer and a YSZ layer have a function as a buffer layer, control a reaction with a superconduction layer, prevent the fall of a superconduction property, and they are arranged in order to maintain adjustment with a superconduction layer. Furthermore, it is  $Y1+XBa2-X Cu3 OY$  on the above-mentioned YSZ layer.  $CeO_2$  which was excellent with crystallographic adjustment with a superconductor (henceforth YBCO) What prepared the thin film can be used as a substrate.

[0025] Furthermore, the compound substrate (henceforth an IBAD compound substrate) using the IBAD method While irradiating ion from across to this nickel system substrate on the tape-like nickel system substrate of high intensity by nonmagnetic (Hastelloy etc.) It is what prepared the interlayers ( $CeO_2$ ,  $Y_2O_3$ , YSZ, etc.) who control a reaction with the element which has the tropism of your kind consideration which was made to deposit the particle generated from the target and was formed, and constitutes a superconductor. What made the above-mentioned interlayer two-layer structure (Rx shows Y, Nd, Sm, Gd, Ei, Yb, Ho, Tm, Dy, Ce, La, or Er. YSZ or  $Zr_2 R X 2O_7 / CeO_2$ ,  $Y_2 O_3$ , etc.): It suits well (JP,4-329867,A, JP,4-331795,A, application for patent No. 333843 [ 2000 to ]).



[0026] Although formation of a thick film is enabled in the invention in this application by performing temporary-quenching heat treatment temperature except the oxide superconductivity precursor of the outermost layer at less than 400 degrees C at least among temporary-quenching heat treatments, for example while forming a two or more layers oxide superconductivity precursor on a substrate. This For example, when the temporary-quenching film of a three-tiered structure is crystallized and oxides superconductors are formed, It means performing preferably less than 400 degrees C of temporary-quenching heat treatment temperature of 1 and a two-layer eye in a 250-350-degree C temperature requirement, and it is satisfactory even if the temporary-quenching heat treatment temperature of the 3rd layer exceeds at least less than 400 degrees C 400 degrees C.

[0027] Moreover, in the invention in this application, although the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere is made into less than [ 4.0vol% ] and is performed for example, in addition to two or more layer formation of a precursor, thick-film-ization is attained also by crystallization of the temporary-quenching film of one layer using a hyperviscous solution in this case.

[0028] In the invention in this application, although it is the thing under heat-of-crystallization processing which makes the steam partial pressure of the introductory gas in the heat-of-crystallization processing ambient atmosphere before crystallization attainment of the oxide superconductivity precursor of the outermost layer less than [ 4.0vol% ], and performs it at least while forming a two or more layers oxide superconductivity precursor on a substrate, for example. This For example, when the temporary-quenching film of a three-tiered structure is crystallized and oxides superconductors are formed, the steam partial pressure of the introductory gas under heat-of-crystallization processing of a 1 and a two-layer eye until crystallization of the 3rd layer is started -- less than [ 4.0vol% ] -- desirable -- the range of 0.5 - 3.2vol% (still more preferably) It means the range of 1.0 - 3.2vol%, and carrying out by coming out. the introductory gas in a heat-of-crystallization processing ambient atmosphere. The mixed gas which consists of the gas and oxygen which do not react with a steam and oxides superconductors is used, and the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere can also raise fixed inclination Shimo or a phase target, if the above conditions are satisfied.

[0029] Moreover, although it is desirable to be carried out by being below a steam partial pressure before crystallization attainment as for the heat-of-crystallization processing after crystallization attainment of the oxide superconductivity precursor of the outermost layer, in order to control degradation of the property by the reaction of a steam and a superconductor, it is desirable [ especially after crystallization termination ] to introduce a dry gas.

[0030]

[Example] As example 1 substrate, the LAO single crystal substrate with die length of 10mm, a width of face [ of 10mm ], and a thickness of 0.5mm was used.

[0031] On this substrate, each metal TFA salt was dissolved in the methanol so that the mole ratio of Y:Ba:Cu might be set to 1:2:3, solution concentration was adjusted [ 1. ] in 0.25 mols /by Y conversion, and the raw material solution was created.

[0032] This raw material solution was applied with the spin coat method on the substrate, and the spreading film was formed. Thus, after having carried out furnace cooling after heating to 300 degrees C with a low programming rate under the oxygen ambient atmosphere containing a steam to the spreading film on the obtained substrate, applying the raw material solution further by the approach same subsequently again as the above and forming the spreading film, it heated to 400 degrees C with the low programming rate under the oxygen ambient atmosphere containing a steam, subsequently furnace cooling was carried out, and the Y-Ba-Cu precursor was obtained.

[0033] In the heat-of-crystallization processing following this temporary-quenching heat treatment, the above-mentioned precursor film was heated with the programming rate of 25 degrees C / min under the hypoxia ambient atmosphere of 10-3atm containing a steam, substrate temperature was maintained at 750 degrees C, and after heat-of-crystallization processing, furnace cooling was carried out, after changing the furnace atmosphere subsequently to a dry gas and holding for 10 minutes.

[0034] In the above case, the steam was introduced in the furnace by carrying out bubbling of the inside of the flask into which 30-degree C deionized water went introductory gas. Moreover, the thickness of the superconductor obtained by one spreading is about 0.2 micrometers.

[0035] On the film obtained as mentioned above, silver was vapor-deposited, the electrode was formed, heat treatment was performed at 450 degrees C in the oxygen ambient atmosphere for 1 hour, and the superconduction film was formed.

[0036] As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0037] About this superconduction film, Tc was measured by the direct-current 4 terminal method. Moreover, with the YBCO (102) pole figure, the c-axis and the rate of a-axis orientation were measured. The measurement result of Tc at the time of using a LAO single crystal substrate, a c-axis, and the rate of a-axis orientation is shown in Table 1.

[0038]

[Table 1]

	実施例 1	比較例 1	
基板	L A O 単結晶基板		
塗布回数 (回)	2	1	2
膜厚 (μ m)	0. 4	0. 2	0. 4
仮焼温度 (1 回目 : °C)	3 0 0	4 0 0	4 0 0
仮焼温度 (2 回目 : °C)	4 0 0	—	4 0 0
c 軸配向率 (%)	8 0	9 5	5 0
a 軸配向率 (%)	2 0	5	5 0
T c (K)	9 2	9 2	8 6

[0039] The raw material solution was applied on the substrate using the LAO single crystal substrate by the same approach as example of comparison 1 example 1, and the spreading film was formed. Thus, after heating to 400 degrees C with a low programming rate under the oxygen ambient atmosphere containing a steam to the spreading film on the obtained substrate, furnace cooling was carried out and the Y-Ba-Cu precursor was obtained (count 1 of spreading). Furthermore, after heating to 400 degrees C with a low programming rate under the oxygen ambient atmosphere which contained the steam after applying the raw material solution by the same approach as the above and forming the spreading film on this temporary-quenching film separately again, furnace cooling was carried out and the Y-Ba-Cu precursor was obtained (count 2 of spreading). To two kinds of these Y-Ba-Cu precursors, henceforth, by the same approach as an example 1, the superconductor was formed on the LAO single crystal substrate.

[0040] As for this superconduction film, it was checked as a result of the X diffraction that YBCO of all is a principal component.

[0041] About this superconduction film, Tc, the c-axis, and the rate of a-axis orientation were measured like the example 1. The result was shown in Table 1 at coincidence.

[0042] as example 2 substrate -- Hastelloy / YSZ/CeO2 from -- the becoming IBAD compound substrate was used. this compound substrate -- about 10nm average crystal grain -- having -- the Hastelloy with die-length [ of 10mm ]; width-of-face [ of 10mm ], and a thickness of 0.1mm tape top -- IBAD -- law -- using -- the bottom of a room temperature -- the 1st interlayer of YSZ -- the thickness of 1 micrometer -- forming membranes -- a this top -- the sputtering method -- using -- CeO2 The 2nd interlayer was formed and created in thickness of 0.5 micrometers.

[0043] By the same approach as an example 1, the superconductor was formed on the compound substrate except having used this compound substrate. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0044] About this superconduction film,  $T_c$ , the c-axis, and the rate of a-axis orientation were measured like the example 1. A result is shown in Table 2.

[0045]

[Table 2]

	実施例 2	比較例 2	
基板	I B A D 複合基板		
塗布回數 (回)	2	1	2
膜厚 (μ m)	0. 4	0. 2	0. 4
仮焼温度 (1 回目 : ℃)	3 0 0	4 0 0	4 0 0
仮焼温度 (2 回目 : ℃)	4 0 0	—	4 0 0
c 軸配向率 (%)	7 4	9 0	4 0
a 軸配向率 (%)	2 6	1 0	6 0
T c (K)	9 2	9 2	8 4

[0046] as example of comparison 2 substrate -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- by the same approach as the example 1 of a comparison, two kinds of superconductors were formed on the IBAD compound substrate except having used the becoming IBAD compound substrate. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0047] About this superconduction film,  $T_c$ , the c-axis, and the rate of a-axis orientation were measured like the example 1. The result was shown in Table 2.

[0048] Even when which substrate is used as compared with the case where the case where temporary-quenching heat treatment of the 1st layer is performed at 300 degrees C is performed at 400 degrees C when the temporary-quenching film is formed in two-layer so that clearly [ the above example 1 and 2 lists ] from the result of the examples 1 and 2 of a comparison, while  $T_c$  improves, it is admitted that the rate of c-axis orientation is improving remarkably. Although the rate of c-axis orientation falls as compared with the case where these values form the temporary-quenching film in one layer, it is shown that  $T_c$  is in equivalent level.

[0049] When the temporary-quenching film is formed in one layer or two-layer and temporary-quenching heat treatment is performed at 400 degrees C, while  $T_c$  falls [ the two-layer temporary-quenching film ] from 92K to 84-86K to the temporary-quenching film of one layer, the rate of c-axis orientation also falls remarkably.

[0050] It is thought that this cause is because the epitaxial growth from a substrate is barred by generation of the 1st layer and the impurity layer of the interface of the two-layer eye at the time of heat-of-crystallization processing. As a factor of generation of this impurity layer, when temporary-quenching heat treatment temperature is high, crystallization in the amorphous precursor film advances, the 1st layer, the temporary-quenching film, and crystal grain of a two-layer eye react preferentially at the time of heat-of-crystallization processing, and it is thought that it becomes easy to generate an impurity.

[0051] Moreover, when temporary-quenching heat treatment of the 1st layer is made low and the temporary-quenching film is formed in two-layer from the result of the above examples 1 and 2, most differences are not accepted in  $T_c$  and the rate of c-axis orientation between the cases where the case where a single crystal is used as a substrate, and an IBAD compound substrate are used. Furthermore, most differences by  $T_c$  at the time of forming the temporary-quenching film in one layer and the substrate of the rate of c-axis orientation are not accepted from the result of the examples 1 and 2 of a comparison.

[0052] The steam partial pressure (1.05vol%) and the heat-of-crystallization processing time of introductory gas in an example 3 heat-of-crystallization processing ambient atmosphere were changed,

and also temporary quenching was carried out at 300 degrees C by the same approach as an example 1, temporary quenching was carried out at 400 more degrees C, on the LAO single crystal substrate, the temporary-quenching film was formed in one layer or two-layer, subsequently heat-of-crystallization processing was performed and the superconduction film was formed. Moreover, the example which carried out temporary quenching to four layers at 300 degrees C, and carried out temporary quenching of the 5th layer at 400 degrees C was also shown in coincidence. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0053]  $J_c$  value and  $I_c$  value (electrical-potential-difference criteria 1 microvolt/cm) of this superconduction film were measured by the direct-current 4 terminal method. Moreover, it asked for the integrated intensity and half-value width of a peak corresponding to a YBCO (005) side according to the X diffraction (rocking curve). A result is shown in Table 3.

[0054]

[Table 3]

	実施例 3			比較例 3		
基板	LAO単結晶基板					
水蒸気分圧 (vol%)	1. 0 5	1. 0 5	1. 0 5	4. 2	4. 2	4. 2
熱処理時間 (min)	6 0	1 8 0	3 0 0	6 0	6 0	1 2 0
塗布回数 (回)	1	2	5	1	2	5
膜厚 (μm)	0. 2	0. 4	1. 0	0. 2	0. 4	1. 0
J c (MA/cm2 )	4	3	2	3. 7	1. 3	0. 4
I o (A)	8 0	1 2 0	2 0 0	7 4	5 2	4 0
ピーク積分強度	11448	18258	32628	9714	11574	15238
半値幅 (deg.)	0. 3 3	0. 5 7	0. 6 2	0. 3 8	0. 7 1	0. 9 5

( $J_c$ : 77 K)

[0055] The steam partial pressure (4.2vol%) and heat treatment time amount of introductory gas in an example of comparison 3 heat-of-crystallization processing ambient atmosphere were changed, and also temporary quenching was carried out at 300 degrees C by the same approach as an example 1, temporary quenching was carried out at 400 more degrees C, on the LAO single crystal substrate, the temporary-quenching film was formed in one layer, two-layer, or five layers, subsequently heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0056]  $J_c$  value,  $I_c$  value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. The result was shown in Table 3.

[0057] When forming the temporary-quenching film in one layer and changing a steam partial pressure to 1.05vol(s)% or 4.2vol(s)% so that clearly from the result of the above example 3 and the example 3 of a comparison, the difference is small although some  $J_c$  values and  $I_c$  values change.

[0058] Moreover, the temporary-quenching film is formed in two-layer, and when a steam partial pressure is reduced with 1.05vol(s)% and heat-of-crystallization processing is performed, although some  $J_c$  values fall,  $I_c$  value increases about 1.5 times as compared with the case where the temporary-quenching film is formed in one layer.

[0059] On the other hand, when the temporary-quenching film was formed in two-layer and heat-of-crystallization processing was performed for a steam partial pressure at 4.2vol(s)%, when  $J_c$  value falls remarkably as compared with the case where the temporary-quenching film is formed in one layer, the result to which  $I_c$  value also falls is shown, and decline in the rate of c-axis orientation of YBCO was checked from the rocking curve in this case.

[0060] Since the crystal growth rate of the YBCO film will become large if the steam partial pressure at the time of heat-of-crystallization processing increases, the above result is considered to be because for crystallinity and the rate of c-axis orientation to fall.

[0061] Formed the thick film by one spreading with the high-concentration raw material solution which adjusted [1.] example 4 solution concentration in 0.63 mols /, and the steam partial pressure (1.05vol%)

and heat treatment time amount of introductory gas in a heat-of-crystallization processing ambient atmosphere were changed, and also temporary quenching was carried out at 400 degrees C by the same approach as an example 1, on the LAO single crystal substrate, 1 stratification of the temporary-quenching film of a thick film was carried out, subsequently heat-of-crystallization processing was performed, and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0062]  $J_c$  value,  $I_c$  value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. A result is shown in Table 4.

[0063]

[Table 4]

	実施例 4	比較例 4
基板	L A O 単結晶基板	
水蒸気分圧 (vol%)	1. 0 5	4. 2
熱処理時間 (min)	1 8 0	6 0
塗布回数 (回)	1	1
膜厚 ( $\mu m$ )	0. 5	0. 5
$J_c$ (MA/cm <sup>2</sup> )	2. 4	0. 6
$I_c$ (A)	1 2 0	3 0
ピーク積分強度	2 0 1 3 4	9 8 7 6
半値幅 (deg.)	0. 6	0. 8 2

( $J_c$  : 7 7 K)

[0064] formed the thick film by one spreading with the high-concentration raw material solution which adjusted [ 1. ] example of comparison 4 solution concentration in 0.63 mols /, and the steam partial pressure (4.2vol%) and heat treatment time amount of introductory gas in a heat of crystallization processing ambient atmosphere be changed , and also temporary quenching be carried out at 400 degrees C by the same approach as an example 1 , on the LAO single crystal substrate , 1 stratification of the temporary quenching film be carried out , subsequently heat of crystallization processing be performed , and the superconduction film be formed . As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0065]  $J_c$  value,  $I_c$  value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. The result was shown in Table 4.

[0066] Enlarge concentration of a raw material solution and the temporary-quenching film of a thick film (0.5 micrometers) is formed in one layer so that clearly from the result of the above example 4 and the example 4 of a comparison. When a steam partial pressure is reduced with 1.05vol(s)% and heat-of-crystallization processing is performed, although  $J_c$  value falls to about 60%,  $I_c$  value increases about 1.5 times as compared with the case where the temporary-quenching film is formed in one layer with a thickness of 0.2 micrometers (example 3 reference).

[0067] on the other hand, enlarge concentration of a raw material solution, form the temporary-quenching film of a thick film (0.5 micrometers) in one layer, and when heat-of-crystallization processing is performed at 4.2vol(s)%, a steam partial pressure As compared with the case where the temporary-quenching film is formed in one layer with a thickness of 0.2 micrometers (example of comparison 3 reference), the result which  $J_c$  value and  $I_c$  value are also large, and falls is shown, and decline in the rate of c-axis orientation of YBCO was checked from the rocking curve in this case.

[0068] If the steam partial pressure at the time of heat-of-crystallization processing also increases this reason, the crystal growth rate of the YBCO film will become large, and it will think for crystallinity and the rate of c-axis orientation to fall.

[0069] the LAO single crystal substrate of example 5 example 3 -- replacing with -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- the becoming IBA compound substrate was used, and also the temporary-quenching film was formed in one layer or two-layer on this compound substrate by the same approach as an example 3, subsequently heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X

diffraction that YBCO is a principal component.

[0070]  $J_c$  value,  $I_c$  value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. A result is shown in Table 5.

[0071]

[Table 5]

	実施例 5		比較例 5	
基板	I B A D 複合基板			
水蒸気分圧 (vol%)	1. 0 5	1. 0 5	4. 2	4. 2
熱処理時間 (min)	6 0	1 8 0	6 0	6 0
塗布回数 (回)	1	2	1	2
膜厚 (μm)	0. 2	0. 4	0. 2	0. 4
J <sub>c</sub> (MA/cm <sup>2</sup> )	3	2. 3	2. 4	0. 7
I <sub>c</sub> (A)	6 0	9 0	4 8	2 8
ピーク積分強度	8586	13693	6301	7507
半値幅 (deg.)	0. 3 3	0. 6 0	0. 4 5	1. 1 0

( $J_c$  : 7 7 K)

[0072] the LAO single crystal substrate of example of comparison 5 example 3 -- replacing with -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- the becoming IBAD compound substrate was used, and also the temporary-quenching film was formed in one layer or two-layer on this compound substrate by the same approach as the example 3 of a comparison, subsequently heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0073]  $J_c$  value,  $I_c$  value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. The result was shown in Table 5.

[0074] the LAO single crystal substrate of example 6 example 3 -- replacing with -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- by the same approach as an example 4, the becoming IBAD compound substrate was used, and also the thick film was formed by one spreading using the high-concentration raw material solution, heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0075]  $J_c$  value,  $I_c$  value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. A result is shown in Table 6.

[0076]

[Table 6]

	実施例 6	比較例 6
基板	I B A D 複合基板	
水蒸気分圧 (vol%)	1. 0 5	4. 2
熱処理時間 (min)	1 8 0	6 0
塗布回数 (回)	1	1
膜厚 ( $\mu m$ )	0. 5	0. 5
$J_c$ ( $MA/cm^2$ )	1. 8	0. 5
$I_c$ (A)	9 0	2 5
ピーク積分強度	1 5 4 3 2	6 9 3 7
半値幅 (deg.)	0. 6 5	1. 3

( $J_c$  : 7 7 K)

[0077] the LAO single crystal substrate of example of comparison 6 example 3 -- replacing with -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- by the same approach as the example 4 of a comparison, the becoming IBAD compound substrate was used, and also the thick film was formed by one spreading using the high-concentration raw material solution, heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the

X diffraction that YBCO is a principal component.

[0078]  $J_c$  value,  $I_c$  value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. The result was shown in Table 6.

[0079] Although  $J_c$  value and  $I_c$  value fell to the example 3 and 4 lists to which the result of the examples 5 and 6 of a comparison used the LAO single crystal substrate for the above example 5 and 6 lists using a compound substrate, respectively as compared with the examples 3 and 4 of a comparison, the result which shows the same inclination was obtained.

[0080]

[Effect of the Invention] As stated above, according to this invention, the tape-like oxides superconductors of a thick film which have the tropism of your kind consideration and a high  $J_c$  value are obtained by controlling the temporary-quenching heat treatment temperature at the time of heat treatment of the oxide superconductivity precursor formed on the substrate, and/or the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere. Moreover, in order that it may form a superconduction layer by the MOD method which is a gassiness process while heat-of-crystallization processing of one layer or the temporary-quenching spreading film of multilayer structure can attain it, thick-film-ization of these oxides superconductors is suitable for a long wire rod, can reduce that manufacturing cost remarkably and is suitable for the application to a superconduction magnet or a superconduction cable.

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[Translation done.]

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the thick-film tape-like oxides superconductors which are built over an oxide superconductivity object and its manufacture approach, especially are suitable for wire rod-ization applicable to a superconduction magnet, a superconduction cable, a power device, etc., and its manufacture approach.

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PRIOR ART

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[Description of the Prior Art] Since, as for oxides superconductors, the critical temperature ( $T_c$ ) exceeds liquid nitrogen temperature, the application to a superconduction magnet, a superconduction cable, a power device, etc. is expected, and various researches are advanced wholeheartedly.

[0003] In order to apply oxide super-\*\*\*\* to the above-mentioned field, critical current density ( $J_c$ ) is high, and it is necessary to manufacture a long wire rod, and on the other hand, in order to obtain a long tape, it is necessary to form oxide super-\*\*\*\* on a metal tape from reinforcement and a flexible viewpoint.

[0004] Moreover, since a superconduction property changes with those crystallographic directions, oxides superconductors need to raise the stacking tendency within a field, and, also for this reason, need to form oxides superconductors on a tape-like substrate. In this case, in order to raise critical current density, it is necessary to carry out orientation of the c-axis of oxides superconductors at right angles to the plate surface of a substrate, and to carry out orientation within a field of that a-axis (or b-axis) almost in parallel with the direction of a current, and to hold the quantum affinity of a superconducting state good.

[0005] (Tape-like RE system oxides superconductors (RE shows at least one or more sorts of elements chosen from Y, Nd, Sm, Gd, Eu, Yb, Pr, or Ho here.), i.e.,  $RE_{1+X}Ba_{2-X}Cu_3O_Y$ ) It is below the same. The MOD method is learned as the manufacture approach of system oxides superconductors.

[0006] This MOD method (Metal Organic Deposition Processes: the organic-acid salt depositing method) After applying on a substrate the solution which is made to carry out the pyrolysis of the metal organic-acid salt, and dissolved the organic compound of a metal component in homogeneity, It is the approach of forming a thin film on a substrate by heating and carrying out the pyrolysis of this, high  $J_c$  is obtained in a gassiness process, and also by low cost, since high-speed membrane formation is possible, it has an advantage suitable for manufacture of the oxide superconductivity wire rod of the shape of a long tape.

[0007] In the MOD method, although the carbonate of alkaline earth metal (Ba etc.) will usually be generated if the pyrolysis of the metal organic-acid salt which is a start raw material is carried out, elevated-temperature heat treatment of 800 degrees C or more is needed for formation of the oxides superconductors by the solid phase reaction which goes via this carbonate. Therefore, the organic-acid salt (for example, a TFA salt: trifluoroacetic acid salt) containing a fluorine is used as a start raw material, and the approach of forming RE (123) superconductor (it being the same RE:Ba:Cu=1:2:3 and the following.) by heat treatment in a steam ambient atmosphere and control of a steam partial pressure is performed energetically in recent years.

[0008] The approach of using this TFA salt as a start raw material can be done [ not producing a nucleation in a solution but carrying out epitaxial growth of the RE (123) superconductor from a substrate by the reaction of a steam and the amorphous precursor containing a fluorine, or ].

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EFFECT OF THE INVENTION

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[Effect of the Invention] As stated above, according to this invention, the tape-like oxides superconductors of a thick film which have the tropism of your kind consideration and a high  $J_c$  value are obtained by controlling the temporary-quenching heat treatment temperature at the time of heat treatment of the oxide superconductivity precursor formed on the substrate, and/or the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere. Moreover, in order that it may form a superconduction layer by the MOD method which is a gassiness process while heat-of-crystallization processing of one layer or the temporary-quenching spreading film of multilayer structure can attain it, thick-film-ization of these oxides superconductors is suitable for a long wire rod, can reduce that manufacturing cost remarkably and is suitable for the application to a superconduction magnet or a superconduction cable.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] As mentioned above, when manufacturing tape-like oxides superconductors by the MOD method, for utilization, thick-film-izing for raising a critical current value ( $I_c$ ) is indispensable. Although it is possible to make high viscosity of the raw material solution containing a TFA salt, and to thicken the spreading film in order to attain this thick-film-ization for a TFA salt by the MOD method used as a start raw material HF and CO<sub>2</sub> which will carry out decomposition generation at the time of temporary quenching if the thickness applied at once becomes thick. When the amount of gas increases, the phenomenon in which the spreading film disperses arises and the tape-like oxides superconductors of a thick film cannot be manufactured as a result.

[0010] Moreover, although it is possible to repeat the process of spreading and temporary quenching and to thicken the spreading film, it becomes difficult by heat-of-crystallization processing to make the superconduction crystal excellent in the stacking tendency within a field generate on a substrate in this case. It is thought that it is because the nucleation used as the nucleus of crystal growth produces this reason into parts other than a substrate side.

[0011] This invention sets it as the purpose to offer the tape-like oxides superconductors and its manufacture approach of the thick film which has the tropism of your kind consideration, and a high  $J_c$  value by having been made in order to solve the above trouble, and controlling the temporary-quenching heat treatment temperature at the time of heat treatment of the oxide superconductivity precursor formed on the substrate, and/or the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere.

[0012] Heat-of-crystallization processing of one layer or the temporary-quenching spreading film of multilayer structure can attain thick-film-ization of these oxides superconductors.

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MEANS

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[Means for Solving the Problem] In order to attain the above purpose, invention concerning this application claim 1, i.e., thick-film tape-like oxides superconductors In the oxides superconductors which performed heat-of-crystallization processing to the oxide superconductivity precursor which applied on the substrate the mixed solution of the metal organic-acid salt which contains each metallic element which constitutes oxides superconductors by the predetermined mole ratio, and performed temporary-quenching heat treatment It is made for critical current density [ in / in the thickness of the oxides superconductors after heat-of-crystallization processing / 77K ] to have 0.7 MA/cm<sup>2</sup> by 0.5 micrometers or more.

[0014] As for the above-mentioned oxide superconductivity precursor, it is desirable from the point of crystal growth to control so that the particle size of the crystallized oxide which exists in the film, and a fluoride is 0.3 micrometers or less.

[0015] Moreover, thick-film-ization can be more easily attained by forming the two or more layers above-mentioned oxide superconductivity precursor on a substrate.

[0016] It is desirable that the temporary-quenching heat treatment temperature except the oxide superconductivity precursor of the outermost layer performs the above-mentioned temporary-quenching heat treatment at less than 400 degrees C at least, and it is desirable especially that it is the range whose temporary-quenching heat treatment temperature is 250-350 degrees C.

[0017] Furthermore, it is desirable that a steam partial pressure performs heat-of-crystallization processing in the ambient atmosphere not more than 4.0vol%, and it is desirable that it is in the range (range whose steam partial pressure is 1.0 - 3.2vol% still more preferably) whose steam partial pressure is 0.5 - 3.2vol% especially. In this case, the result of having excelled more for performing the steam partial pressure in the heat-of-crystallization processing ambient atmosphere before crystallization attainment of the oxide superconductivity precursor of the outermost layer at least in 0.5 - 3.2vol% (range whose steam partial pressure is 1.0 - 3.2vol% still more preferably), and being below a steam partial pressure before crystallization attainment, and performing heat-of-crystallization processing after crystallization attainment of the oxide superconductivity precursor of the outermost layer is obtained.

[0018] The above heat-of-crystallization processing is performed in the ambient atmosphere which introduced the mixed gas which consists of the gas and oxygen which do not react with a steam and oxides superconductors.

[0019] Although oxides superconductors are formed considering the mixed solution of a metal organic-acid salt as a start raw material, as for this metal organic-acid salt, it is desirable to consist of any one or more sorts of a trifluoroacetic acid salt, an octylic acid salt, naphthenate, or acetate, and it is more desirable that a trifluoroacetic acid salt is included especially at least.

[0020] invention which the oxides superconductors described above require for this application claim 14, i.e., RE<sub>1</sub>+X Ba<sub>2</sub>-X Cu<sub>3</sub> OY, from, after applying the mixed solution of the metal organic-acid salt which contains each metallic element which constitutes the becoming oxides superconductors by the predetermined mole ratio on a substrate In the approach of forming an oxide superconductivity precursor, crystallizing an oxide superconductivity precursor by subsequently performing heat-of-

crystallization processing, and manufacturing oxides superconductors by performing temporary-quenching heat treatment While forming a two or more layers oxide superconductivity precursor on a substrate, temporary-quenching heat treatment temperature except the oxide superconductivity precursor of the outermost layer is performed at less than 400 degrees C at least among temporary-quenching heat treatments. And it can manufacture by making the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere into less than [ 4.0vol% ], and performing it. [0021] In this case, it is desirable that it is the range whose temporary-quenching heat treatment temperature is 250-350 degrees C, and is the range whose steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere is 0.5 - 3.2vol%, and it is desirable especially that it is the range whose steam partial pressure is 1.0 - 3.2vol%.

[0022]

[Embodiment of the Invention] As a substrate used in this invention, either a single crystal substrate or a polycrystal substrate can be used.

[0023] as a single crystal substrate -- a LaAlO<sub>3</sub> single-crystal (100) substrate (henceforth a LAO single crystal substrate) etc. -- it can use -- on the other hand -- as a polycrystal substrate -- a stacking tendency nickel substrate and IBAD -- the compound substrate using law (Ion Beam Assisted Deposition) etc. can be used.

[0024] A stacking tendency nickel substrate heat-treats and carries out high orientation of the nickel substrate which carried out cold working in a vacuum, is developed in U.S. Oak Ridge National Laboratory, and is called RABiTS (trademark: rolling-assisted biaxially textured-substrates). It is CeO<sub>2</sub> by making a cerium deposit by EB evaporation in a hot inert gas ambient atmosphere on this stacking tendency nickel substrate, and making a steam exist during this deposition. The thin film of an epitaxial layer can be prepared and what formed the thick film of YSZ (yttrium fully stabilized zirconia) under elevated-temperature reduced pressure by the sputtering method on it further can be used as a substrate. This CeO<sub>2</sub> A layer and a YSZ layer have a function as a buffer layer, control a reaction with a superconduction layer, prevent the fall of a superconduction property, and they are arranged in order to maintain adjustment with a superconduction layer. Furthermore, it is Y<sub>1</sub>+XBa<sub>2</sub>-X Cu<sub>3</sub> O<sub>Y</sub> on the above-mentioned YSZ layer. CeO<sub>2</sub> which was excellent with crystallographic adjustment with a superconductor (henceforth YBCO) What prepared the thin film can be used as a substrate.

[0025] Furthermore, the compound substrate (henceforth an IBAD compound substrate) using the IBAD method While irradiating ion from across to this nickel system substrate on the tape-like nickel system substrate of high intensity by nonmagnetic (Hastelloy etc.) It is what prepared the interlayers (CeO<sub>2</sub>, Y<sub>2</sub> O<sub>3</sub>, YSZ, etc.) who control a reaction with the element which has the tropism of your kind consideration which was made to deposit the particle generated from the target and was formed, and constitutes a superconductor. What made the above-mentioned interlayer two-layer structure (Rx shows Y, Nd, Sm, Gd, Ei, Yb, Ho, Tm, Dy, Ce, La, or Er. YSZ or Zr<sub>2</sub> R X 2O<sub>7</sub> / CeO<sub>2</sub>, Y<sub>2</sub> O<sub>3</sub>, etc.:) It suits well (JP,4-329867,A, JP,4-331795,A, application for patent No. 333843 [ 2000 to ]).

[0026] Although formation of a thick film is enabled in the invention in this application by performing temporary-quenching heat treatment temperature except the oxide superconductivity precursor of the outermost layer at less than 400 degrees C at least among temporary-quenching heat treatments, for example while forming a two or more layers oxide superconductivity precursor on a substrate This For example, when the temporary-quenching film of a three-tiered structure is crystallized and oxides superconductors are formed, It means performing preferably less than 400 degrees C of temporary-quenching heat treatment temperature of 1 and a two-layer eye in a 250-350-degree C temperature requirement, and it is satisfactory even if the temporary-quenching heat treatment temperature of the 3rd layer exceeds at least less than 400 degrees C 400 degrees C.

[0027] Moreover, in the invention in this application, although the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere is made into less than [ 4.0vol% ] and is performed for example, in addition to two or more layer formation of a precursor, thick-film-ization is attained also by crystallization of the temporary-quenching film of one layer using a hyperviscous solution in this case.

[0028] In the invention in this application, although it is the thing under heat-of-crystallization processing which makes the steam partial pressure of the introductory gas in the heat-of-crystallization processing ambient atmosphere before crystallization attainment of the oxide superconductivity precursor of the outermost layer less than [ 4.0vol% ], and performs it at least while forming a two or more layers oxide superconductivity precursor on a substrate, for example This For example, when the temporary-quenching film of a three-tiered structure is crystallized and oxides superconductors are formed, the steam partial pressure of the introductory gas under heat-of-crystallization processing of a 1 and a two-layer eye until crystallization of the 3rd layer is started -- less than [ 4.0vol% ] -- desirable -- the range of 0.5 - 3.2vol% (still more preferably) It means the range of 1.0 - 3.2vol%, and carrying out by coming out. the introductory gas in a heat-of-crystallization processing ambient atmosphere The mixed gas which consists of the gas and oxygen which do not react with a steam and oxides superconductors is used, and the steam partial pressure of the introductory gas in a heat-of-crystallization processing ambient atmosphere can also raise fixed inclination Shimo or a phase target, if the above conditions are satisfied.

[0029] Moreover, although it is desirable to be carried out by being below a steam partial pressure before crystallization attainment as for the heat-of-crystallization processing after crystallization attainment of the oxide superconductivity precursor of the outermost layer, in order to control degradation of the property by the reaction of a steam and a superconductor, it is desirable [ especially after crystallization termination ] to introduce a dry gas.

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[Translation done.]

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EXAMPLE

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[Example] As example 1 substrate, the LAO single crystal substrate with die length of 10mm, a width of face [ of 10mm ], and a thickness of 0.5mm was used.

[0031] On this substrate, each metal TFA salt was dissolved in the methanol so that the mole ratio of Y:Ba:Cu might be set to 1:2:3, solution concentration was adjusted [ 1. ] in 0.25 mols /by Y conversion, and the raw material solution was created.

[0032] This raw material solution was applied with the spin coat method on the substrate, and the spreading film was formed. Thus, after having carried out furnace cooling after heating to 300 degrees C with a low programming rate under the oxygen ambient atmosphere containing a steam to the spreading film on the obtained substrate, applying the raw material solution further by the approach same subsequently again as the above and forming the spreading film, it heated to 400 degrees C with the low programming rate under the oxygen ambient atmosphere containing a steam, subsequently furnace cooling was carried out, and the Y-Ba-Cu precursor was obtained.

[0033] In the heat-of-crystallization processing following this temporary-quenching heat treatment, the above-mentioned precursor film was heated with the programming rate of 25 degrees C / min under the hypoxia ambient atmosphere of 10-3atm containing a steam, substrate temperature was maintained at 750 degrees C, and after heat-of-crystallization processing, furnace cooling was carried out, after changing the furnace atmosphere subsequently to a dry gas and holding for 10 minutes.

[0034] In the above case, the steam was introduced in the furnace by carrying out bubbling of the inside of the flask into which 30-degree C deionized water went introductory gas. Moreover, the thickness of the superconductor obtained by one spreading is about 0.2 micrometers.

[0035] On the film obtained as mentioned above, silver was vapor-deposited, the electrode was formed, heat treatment was performed at 450 degrees C in the oxygen ambient atmosphere for 1 hour, and the superconduction film was formed.

[0036] As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0037] About this superconduction film, Tc was measured by the direct-current 4 terminal method. Moreover, with the YBCO (102) pole figure, the c-axis and the rate of a-axis orientation were measured. The measurement result of Tc at the time of using a LAO single crystal substrate, a c-axis, and the rate of a-axis orientation is shown in Table 1.

[0038]

[Table 1]

	実施例 1	比較例 1	
基板	L A O 単結晶基板		
塗布回数 (回)	2	1	2
膜厚 (μ m)	0. 4	0. 2	0. 4
仮焼温度 (1 回目 : °C)	3 0 0	4 0 0	4 0 0
仮焼温度 (2 回目 : °C)	4 0 0	—	4 0 0
c 軸配向率 (%)	8 0	9 5	5 0
a 軸配向率 (%)	2 0	5	5 0
T c (K)	9 2	9 2	8 6

[0039] The raw material solution was applied on the substrate using the LAO single crystal substrate by the same approach as example of comparison 1 example 1, and the spreading film was formed. Thus, after heating to 400 degrees C with a low programming rate under the oxygen ambient atmosphere containing a steam to the spreading film on the obtained substrate, furnace cooling was carried out and the Y-Ba-Cu precursor was obtained (count 1 of spreading). Furthermore, after heating to 400 degrees C with a low programming rate under the oxygen ambient atmosphere which contained the steam after applying the raw material solution by the same approach as the above and forming the spreading film on this temporary-quenching film separately again, furnace cooling was carried out and the Y-Ba-Cu precursor was obtained (count 2 of spreading). To two kinds of these Y-Ba-Cu precursors, henceforth, by the same approach as an example 1, the superconductor was formed on the LAO single crystal substrate.

[0040] As for this superconduction film, it was checked as a result of the X diffraction that YBCO of all is a principal component.

[0041] About this superconduction film, Tc, the c-axis, and the rate of a-axis orientation were measured like the example 1. The result was shown in Table 1 at coincidence.

[0042] as example 2 substrate -- Hastelloy / YSZ/CeO<sub>2</sub> from -- the becoming IBAD compound substrate was used. this compound substrate -- about 10nm average crystal grain -- having -- the Hastelloy with die-length [ of 10mm ], width-of-face [ of 10mm ], and a thickness of 0.1mm tape top -- IBAD -- law -- using -- the bottom of a room temperature -- the 1st interlayer of YSZ -- the thickness of 1 micrometer -- forming membranes -- a this top -- the sputtering method -- using -- CeO<sub>2</sub> The 2nd interlayer was formed and created in thickness of 0.5 micrometers.

[0043] By the same approach as an example 1, the superconductor was formed on the compound substrate except having used this compound substrate. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0044] About this superconduction film, Tc, the c-axis, and the rate of a-axis orientation were measured like the example 1. A result is shown in Table 2.

[0045]

[Table 2]



	実施例 2	比較例 2	
基板	I B A D 複合基板		
膜層回数 (回)	2	1	2
膜厚 (μ m)	0. 4	0. 2	0. 4
仮焼温度 (1 回目 : ℃)	3 0 0	4 0 0	4 0 0
仮焼温度 (2 回目 : ℃)	4 0 0	—	4 0 0
c 軸配向率 (%)	7 4	9 0	4 0
a 軸配向率 (%)	2 6	1 0	6 0
T c (K)	9 2	9 2	8 4

[0046] as example of comparison 2 substrate -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- by the same approach as the example 1 of a comparison, two kinds of superconductors were formed on the IBA D compound substrate except having used the becoming IBA D compound substrate. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0047] About this superconduction film, T<sub>c</sub>, the c-axis, and the rate of a-axis orientation were measured like the example 1. The result was shown in Table 2.

[0048] Even when which substrate is used as compared with the case where the case where temporary-quenching heat treatment of the 1st layer is performed at 300 degrees C is performed at 400 degrees C when the temporary-quenching film is formed in two-layer so that clearly [ the above example 1 and 2 lists ] from the result of the examples 1 and 2 of a comparison, while T<sub>c</sub> improves, it is admitted that the rate of c-axis orientation is improving remarkably. Although the rate of c-axis orientation falls as compared with the case where these values form the temporary-quenching film in one layer, it is shown that T<sub>c</sub> is in equivalent level.

[0049] When the temporary-quenching film is formed in one layer or two-layer and temporary-quenching heat treatment is performed at 400 degrees C, while T<sub>c</sub> falls [ the two-layer temporary-quenching film ] from 92K to 84-86K to the temporary-quenching film of one layer, the rate of c-axis orientation also falls remarkably.

[0050] It is thought that this cause is because the epitaxial growth from a substrate is barred by generation of the 1st layer and the impurity layer of the interface of the two-layer eye at the time of heat-of-crystallization processing. As a factor of generation of this impurity layer, when temporary-quenching heat treatment temperature is high, crystallization in the amorphous precursor film advances, the 1st layer, the temporary-quenching film, and crystal grain of a two-layer eye react preferentially at the time of heat-of-crystallization processing, and it is thought that it becomes easy to generate an impurity.

[0051] Moreover, when temporary-quenching heat treatment of the 1st layer is made low and the temporary-quenching film is formed in two-layer from the result of the above examples 1 and 2, most differences are not accepted in T<sub>c</sub> and the rate of c-axis orientation between the cases where the case where a single crystal is used as a substrate, and an IBA D compound substrate are used. Furthermore, most differences by T<sub>c</sub> at the time of forming the temporary-quenching film in one layer and the substrate of the rate of c-axis orientation are not accepted from the result of the examples 1 and 2 of a comparison.

[0052] The steam partial pressure (1.05vol%) and the heat-of-crystallization processing time of introductory gas in an example 3 heat-of-crystallization processing ambient atmosphere were changed, and also temporary quenching was carried out at 300 degrees C by the same approach as an example 1, temporary quenching was carried out at 400 more degrees C, on the LAO single crystal substrate, the temporary-quenching film was formed in one layer or two-layer, subsequently heat-of-crystallization processing was performed and the superconduction film was formed. Moreover, the example which

carried out temporary quenching to four layers at 300 degrees C, and carried out temporary quenching of the 5th layer at 400 degrees C was also shown in coincidence. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0053] Jc value and Ic value (electrical-potential-difference criteria 1 microvolt/cm) of this superconduction film were measured by the direct-current 4 terminal method. Moreover, it asked for the integrated intensity and half-value width of a peak corresponding to a YBCO (005) side according to the X diffraction (rocking curve). A result is shown in Table 3.

[0054]

[Table 3]

	実施例 3			比較例 3		
基板	LAO単結晶基板					
水蒸気分圧 (vol %)	1. 05	1. 05	1. 05	4. 2	4. 2	
熱処理時間 (min)	60	180	300	60	60	120
塗布回数 (層)	1	2	5	1	2	5
膜厚 (μm)	0. 2	0. 4	1. 0	0. 2	0. 4	1. 0
J c (MA/cm2 )	4	3	2	3. 7	1. 3	0. 4
I c (A)	80	120	200	74	52	40
ピーク積分強度	11448	18258	32628	9714	11574	15238
半値幅 (deg.)	0. 33	0. 57	0. 62	0. 38	0. 71	0. 95

(Jc : 77 K)

[0055] The steam partial pressure (4.2vol%) and heat treatment time amount of introductory gas in an example of comparison 3 heat-of-crystallization processing ambient atmosphere were changed, and also temporary quenching was carried out at 300 degrees C by the same approach as an example 1, temporary quenching was carried out at 400 more degrees C, on the LAO single crystal substrate, the temporary-quenching film was formed in one layer, two-layer, or five layers, subsequently heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0056] Jc value, Ic value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. The result was shown in Table 3.

[0057] When forming the temporary-quenching film in one layer and changing a steam partial pressure to 1.05vol(s)% or 4.2vol(s)% so that clearly from the result of the above example 3 and the example 3 of a comparison, the difference is small although some Jc values and Ic values change.

[0058] Moreover, the temporary-quenching film is formed in two-layer, and when a steam partial pressure is reduced with 1.05vol(s)% and heat-of-crystallization processing is performed, although some Jc values fall, Ic value increases about 1.5 times as compared with the case where the temporary-quenching film is formed in one layer.

[0059] On the other hand, when the temporary-quenching film was formed in two-layer and heat-of-crystallization processing was performed for a steam partial pressure at 4.2vol(s)%, when Jc value falls remarkably as compared with the case where the temporary-quenching film is formed in one layer, the result to which Ic value also falls is shown, and decline in the rate of c-axis orientation of YBCO was checked from the rocking curve in this case.

[0060] Since the crystal growth rate of the YBCO film will become large if the steam partial pressure at the time of heat-of-crystallization processing increases, the above result is considered to be because for crystallinity and the rate of c-axis orientation to fall.

[0061] Formed the thick film by one spreading with the high-concentration raw material solution which adjusted [ 1. ] example 4 solution concentration in 0.63 mols /, and the steam partial pressure (1.05vol%) and heat treatment time amount of introductory gas in a heat-of-crystallization processing ambient atmosphere were changed, and also temporary quenching was carried out at 400 degrees C by the same approach as an example 1, on the LAO single crystal substrate, 1 stratification of the temporary-quenching film of a thick film was carried out, subsequently heat-of-crystallization processing was

performed, and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0062] Jc value, Ic value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. A result is shown in Table 4.

[0063]

[Table 4]

	実施例 4	比較例 4
基板	L A O 単結晶基板	
水蒸気分圧 (vol %)	1. 0 5	4. 2
熱処理時間 (min)	1 8 0	6 0
塗布回数 (回)	1	1
膜厚 (μm)	0. 5	0. 5
J c (MA/cm <sup>2</sup> )	2. 4	0. 6
I c (A)	1 2 0	3 0
ピーク積分強度	2 0 1 3 4	9 8 7 6
半値幅 (deg.)	0. 6	0. 8 2

(J c : 7 7 K)

[0064] formed the thick film by one spreading with the high-concentration raw material solution which adjusted [ 1. ] example of comparison 4 solution concentration in 0.63 mols /, and the steam partial pressure (4.2vol%) and heat treatment time amount of introductory gas in a heat of crystallization processing ambient atmosphere be changed , and also temporary quenching be carried out at 400 degrees C by the same approach as an example 1 , on the LAO single crystal substrate , 1 stratification of the temporary quenching film be carried out , subsequently heat of crystallization processing be performed , and the superconduction film be formed . As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0065] Jc value, Ic value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. The result was shown in Table 4.

[0066] Enlarge concentration of a raw material solution and the temporary-quenching film of a thick film (0.5 micrometers) is formed in one layer so that clearly from the result of the above example 4 and the example 4 of a comparison. When a steam partial pressure is reduced with 1.05vol(s)% and heat-of-crystallization processing is performed, although Jc value falls to about 60%, Ic value increases about 1.5 times as compared with the case where the temporary-quenching film is formed in one layer with a thickness of 0.2 micrometers (example 3 reference).

[0067] on the other hand, enlarge concentration of a raw material solution, form the temporary-quenching film of a thick film (0.5 micrometers) in one layer, and when heat-of-crystallization processing is performed at 4.2vol(s)%, a steam partial pressure As compared with the case where the temporary-quenching film is formed in one layer with a thickness of 0.2 micrometers (example of comparison 3 reference), the result which Jc value and Ic value are also large, and falls is shown, and decline in the rate of c-axis orientation of YBCO was checked from the rocking curve in this case.

[0068] If the steam partial pressure at the time of heat-of-crystallization processing also increases this reason, the crystal growth rate of the YBCO film will become large, and it will think for crystallinity and the rate of c-axis orientation to fall.

[0069] the LAO single crystal substrate of example 5 example 3 -- replacing with -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- the becoming IBAD compound substrate was used, and also the temporary-quenching film was formed in one layer or two-layer on this compound substrate by the same approach as an example 3, subsequently heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0070] Jc value, Ic value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. A result is shown in Table 5.

[0071]

[Table 5]

	実施例 5		比較例 5	
基板	I B A D 複合基板			
水蒸気分圧 (vol %)	1. 0 5	1. 0 5	4. 2	4. 2
熱処理時間 (min)	6 0	1 8 0	6 0	6 0
塗布回数 (回)	1	2	1	2
膜厚 (μm)	0. 2	0. 4	0. 2	0. 4
J c (MA/cm <sup>2</sup> )	3	2. 3	2. 4	0. 7
I c (A)	6 0	9 0	4 8	2 8
ピーク積分強度	8586	13693	6301	7507
半値幅 (deg.)	0. 3 3	0. 6 0	0. 4 5	1. 1 0

(J c : 7 7 K)

[0072] the LAO single crystal substrate of example of comparison 5 example 3 -- replacing with -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- the becoming IBAD compound substrate was used, and also the temporary-quenching film was formed in one layer or two-layer on this compound substrate by the same approach as the example 3 of a comparison, subsequently heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0073] Jc value, Ic value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. The result was shown in Table 5.

[0074] the LAO single crystal substrate of example 6 example 3 -- replacing with -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- by the same approach as an example 4, the becoming IBAD compound substrate was used, and also the thick film was formed by one spreading using the high-concentration raw material solution, heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0075] Jc value, Ic value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. A result is shown in Table 6.

[0076]

[Table 6]

	実施例 6	比較例 6
基板	I B A D 複合基板	
水蒸気分圧 (vol %)	1. 0 5	4. 2
熱処理時間 (min)	1 8 0	6 0
塗布回数 (回)	1	1
膜厚 ( $\mu\text{m}$ )	0. 5	0. 5
J c (MA/cm <sup>2</sup> )	1. 8	0. 5
I c (A)	9 0	2 5
ピーク積分強度	1 5 4 3 2	6 9 3 7
半値幅 (deg.)	0. 6 5	1. 3

(J c : 7 7 K)

[0077] the LAO single crystal substrate of example of comparison 6 example 3 -- replacing with -- Hastelloy / YSZ/CeO<sub>2</sub> of an example 2 from -- by the same approach as the example 4 of a comparison, the becoming IBAD compound substrate was used, and also the thick film was formed by one spreading using the high-concentration raw material solution, heat-of-crystallization processing was performed and the superconduction film was formed. As for this superconduction film, it was checked as a result of the X diffraction that YBCO is a principal component.

[0078] Jc value, Ic value, peak integrated intensity, and half-value width of this superconduction film were measured like the example 3. The result was shown in Table 6.

[0079] Although Jc value and Ic value fell to the example 3 and 4 lists to which the result of the

examples 5 and 6 of a comparison used the LAO single crystal substrate for the above example 5 and 6 lists using a compound substrate, respectively as compared with the examples 3 and 4 of a comparison, the result which shows the same inclination was obtained.

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[Translation done.]